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Arthur Fontijn

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

To help provide a better understanding of - and reliable input data on - gas-phase combustion reactions of B and Aℓ species, experimental measurements were made in a high-temperature fast-flow reactor. The following rate coefficient expressions were obtained (in cubic cm, per molecule, per second units): $BCℓ + O_2 \rightarrow$ Products, $2.2 \times 10(-11)$ exp(-4620 K/T); $BCℓ + CO_2 \rightarrow OBCℓ + CO$, $6.7 \times 10(-13)$ exp(-4500 K/T). A comparison was made to similar reactions involving Aℓ species, reported last year. The radiative lifetime of AℓCℓ (A one pie), of importance to plume models, was determined to be 6.4 ns.

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I. RESEARCH OBJECTIVES

Current ability to improve the combustion efficiency of B and Aℓ solid propellants and slurries is hampered by a lack of understanding and knowledge of the kinetics of the individual reactions involved and the ways and manner by which temperature affects the rate coefficients and product channels. While the simple Arrhenius-type equation $k(T) = AT^{1/2} \exp(-E_A/RT)$ has over limited temperature ranges been of great value, when applied to wide temperature ranges it is often not obeyed. Particularly for exothermic and slightly endothermic reactions, order of magnitude errors can be made by extrapolations based on the Arrhenius equation.[1] It is the goal of this program to provide an insight in the kinetic behavior of B and Aℓ radical oxidation reactions as influenced by temperature. To this end measurements are made in high-temperature fast-flow reactors (HTFFR). These unique tools provide measurements on isolated elementary reactions in a heat bath. With traditional high-temperature techniques, such as flames and shock tubes, such isolation is usually impossible to achieve; as a result, data on any given reaction depend on the knowledge of other reactions occurring simultaneously, leading to large uncertainties. HTFFRs allow kinetic studies from room temperature up to about 2000 K to provide wide range k(T) (temperature-dependent rate coefficient) data.

In the work performed thus far under this grant laser-induced fluorescence LIF has been used to monitor reactant concentrations. The objectives of that work are to measure, over the widest achievable temperature ranges, the kinetics of:

> i) Aℓ, AℓCℓ and BCℓ oxidation reactions, and
>
> ii) oxidation reactions of other simple Aℓ and B-containing radicals, such as AℓO and BO.

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Most tri-atomic products of the oxidation reactions of these monoxides and monohalides have no identified electronic transition spectra and cannot be detected by LIF. To unambiguously establish the kinetics of reactions involving these triatomics and ultimately to develop a good understanding of the reactions leading to the final combustion products, Al_2O_3 and B_2O_3, we have constructed an HTFFR with mass spectrometer detection. This instrument is currently being tested. The first objectives for the work with that apparatus are:

(i)   to identify the products of the $AlCl + O_2$ and $BCl + O_2$ reactions, discussed in Section II, and to determine the temperature dependence of the branching ratio of the AlO_2 and $OAlCl$ product channels of the former reaction, and

(ii)   to resolve the large discrepancy between $\Delta H_f(AlO_2)$ derived from HTFFR-LIF observations and from Knudsen cell mass spectrometry experiments.[2,3]

II. STATUS OF THE RESEARCH EFFORT

In the first year of this grant we have made measurements on several reactions involving $AlCl$. The k(T) data obtained have been reported in the preceding annual report. As an additional Al-study, we have measured the previously unknown radiative lifetime of $AlCl$ $A^1\Pi$ to be 6.4 ns. This latter result has already been incorporated in rocket plume uv band model calculations made at Aerodyne.[4] Most of this $AlCl$ work has now been written up and published;[5-7] a paper on the $Al + Cl_2$, $Al + HCl$ and $AlCl + Cl_2$ reactions is in preparation. In Figure 1 the $AlCl$ k(T) data are compared to results from our previous aluminum oxidation studies involving oxygen oxidizers*.[8]

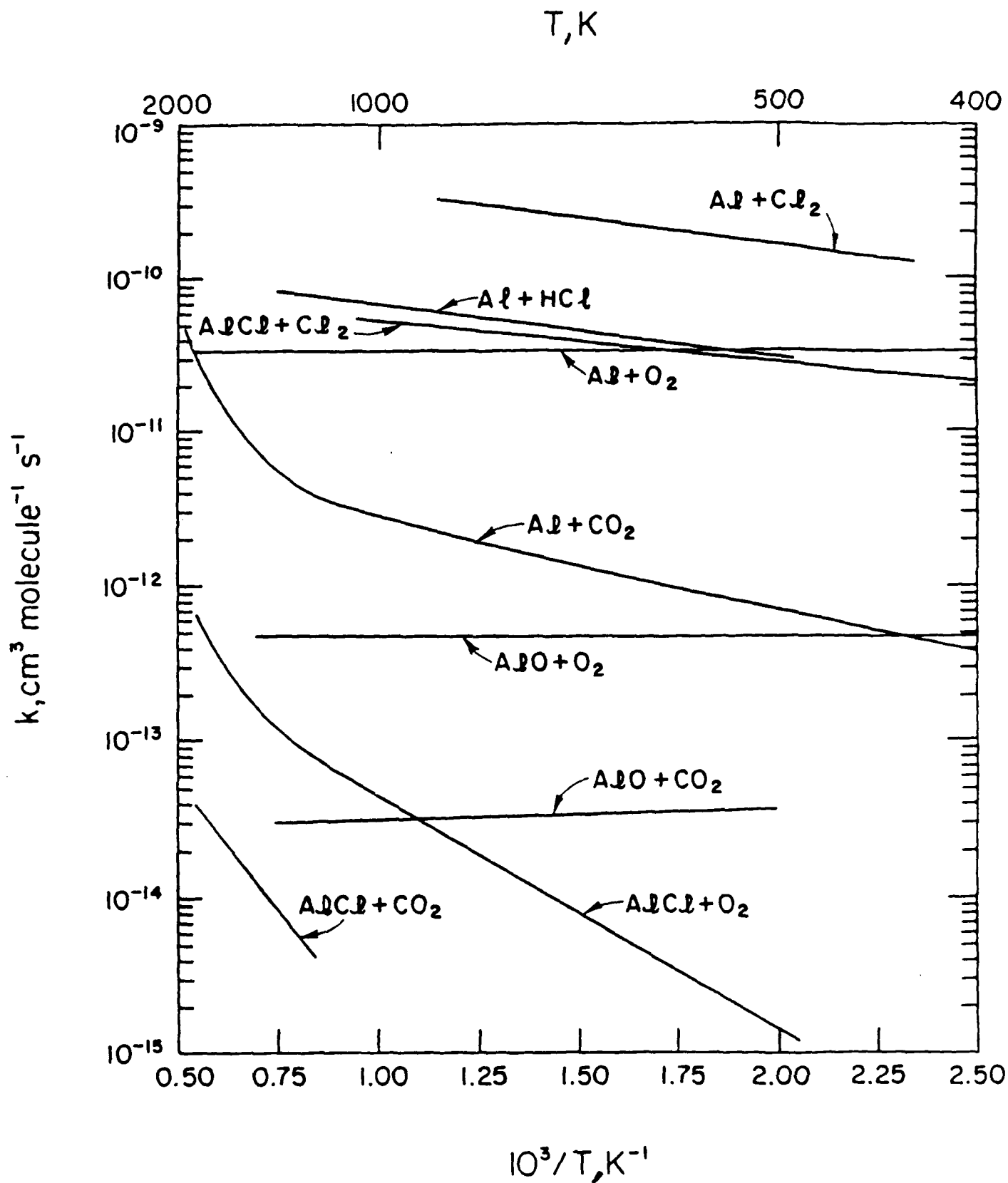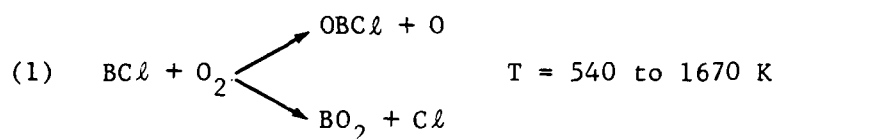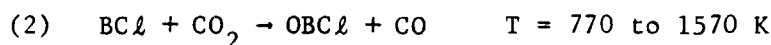* We plan to "complete" this figure by making measurements on the $AlO + Cl_2$ and $AlO + HCl$ reactions.

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Figure 1   Summary of HTFFR Rate Coefficient Measurements on $A\ell/O/C\ell$ Reactions

Together these illustrate the variety of $\ell n k$ vs. T^{-1} dependences observed, the wide range of rate coefficient data that can be measured and the wide range of temperatures that can be covered.

A major breakthrough occurred in the present year when we developed a method for reproducibly introducing a boron species, $BC\ell$, into an HTFFR*. This method, production of $BC\ell$ by passing $B_2H_6/Ar/C\ell_2$ or $HC\ell$ mixtures through a microwave discharge is illustrated in Figure 2. It has led to the following results:

$$(1) \quad BC\ell + O_2 \overset{OBC\ell + O}{\underset{BO_2 + C\ell}{\diagdown}} \qquad T = 540 \text{ to } 1670 \text{ K}$$

$$k_1 = 2.2 \times 10^{-11} \exp(-4620 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$(2) \quad BC\ell + CO_2 \rightarrow OBC\ell + CO \qquad T = 770 \text{ to } 1570 \text{ K}$$

$$k_2 = 6.7 \times 10^{-13} \exp(-4500 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The study of reaction (1) has already been accepted for publication,[10] that of reaction (2) will be written up together with the results from the $BC\ell + C\ell_2$ reaction, now being studied.

In Figure 3 the $BC\ell + O_2$ data are compared to our results[5] on the $A\ell C\ell + O_2$ reaction and those of an earlier study of the $BF + O_2$ reaction over a more limited temperature range (675 to 1035 K).[11] Two observations should be made:

_____

* Our previous attempts at $BC\ell$ production, such as reactive vaporization by passing $BC\ell_3$ or $C\ell_2$ over solid B at $T \geq 1100$ K,[9] led to kinetic data which were a function of reactor parameters.
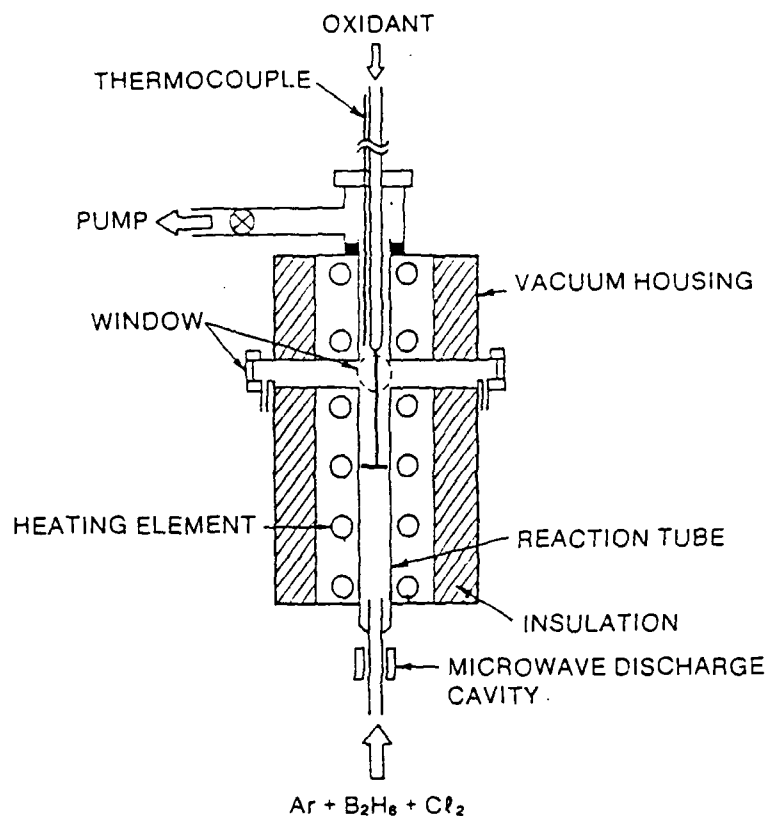
OXIDANT

THERMOCOUPLE

PUMP

VACUUM HOUSING

WINDOW

HEATING ELEMENT

REACTION TUBE

INSULATION

MICROWAVE DISCHARGE CAVITY

Ar + B₂H₆ + Cl₂

Figure 2 Schematic of the HTFFR in use for the LIF Studies of BCℓ Reactions

T, K

2000   1000   500   400

10^{-11}

10^{-12}

10^{-13}

10^{-14}

10^{-15}

10^{-16}

BCℓ + O₂

AℓCℓ + O₂

BF + O₂

k, cm³ molecule⁻¹ s⁻¹

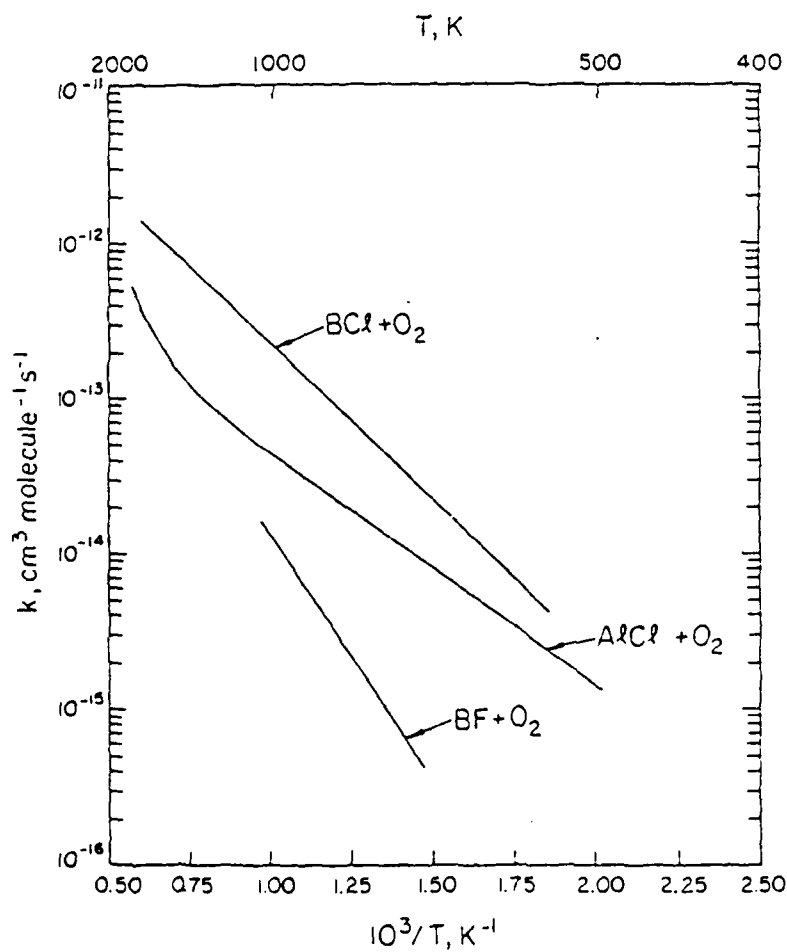0.50 0.75 1.00 1.25 1.50 1.75 2.00 2.25 2.50

$10^3/T$, K⁻¹

Figure 3 Comparison of the $k(T)$ Data of the BCℓ + O₂, AℓCℓ + O₂ and BF + O₂ Reactions

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(i) In the temperature range covered the BCl reaction is faster than the $AlCl$ reaction and considerably faster than the BF reaction. The latter could have important consequences for advanced propellants where fluorine would be a principal species; a similar comparison between the $AlCl + O_2$ and $AlF + O_2$ reactions would appear to be significant for a future HTFFR study.

(ii) Figure 3 shows that while the $AlCl + O_2$ reaction has a sharply curved Arrhenius plot above ≈ 1000 K, the $BCl + O_2$ reaction displays no noticeable deviation from linear ℓn k vs. T^{-1} (normal Arrhenius) behavior. We have speculated that the $AlCl$ plot indicates a transition from an $AlO_2 + Cl$ product channel at the lower temperatures to $OAlCl + O$ at the higher temperatures.[5] The straight line for $BCl + O_2$ suggests that only one channel is operative (one type of product is formed). If this were $OBCl$, the equivalent of the postulated high-temperature Al product, the shape of the two plots would suggest that they may cross, i.e., that at very high temperatures the $AlCl$ reaction could be faster than the BCl reaction. However, if the BCl product is BO_2, the equivalent of the lower temperature Al product, a very fast $BCl + O_2$ reaction may be indicated at high temperatures as sharp upward curvature in the $BCl + O_2$ plot, similar to that of $AlCl + O_2$, would then be a reasonable expectation. Our planned mass spectrometer experiments on the $AlCl + O_2$ and $BCl + O_2$ reactions would provide product indentification and hence should decide between these possibilities.

In Figure 4 we compare the measured rate coefficients of the $BCl + CO_2$ reaction (2) to those we obtained[6] for

(3) $AlCl + CO_2 \rightarrow OAlCl + CO$
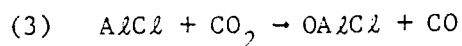
   $k_3 = 2.5 \times 10^{-12} \exp(-7550 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

On thermochemical grounds the products given in Eqs.(2) and (3) are the only possible. While the Al reaction is the slower at the measured temperatures, extrapolation suggests that above about 2300 K it would be the faster reaction.
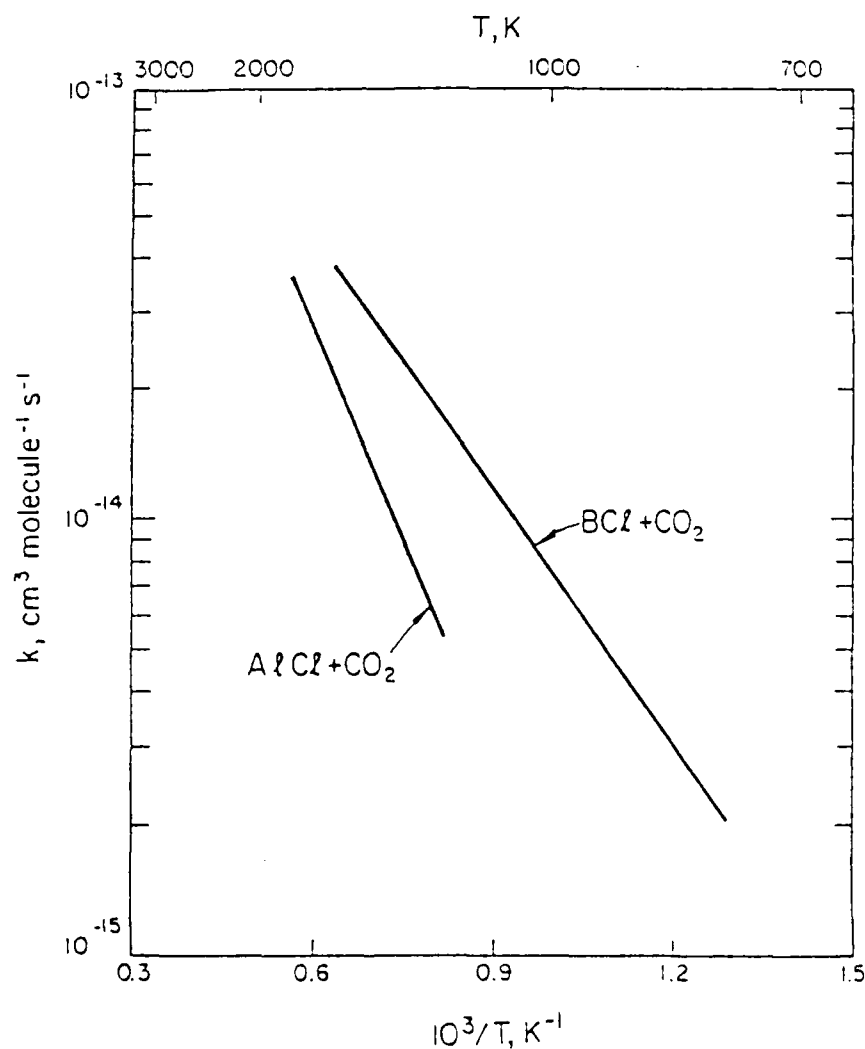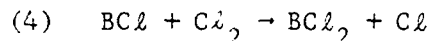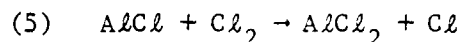

Figure 4 Comparison of the k(T) Data of the $BCl + CO_2$ and $AlCl + CO_2$ Reactions

Our measurements on

$$(4) \quad BC\ell + C\ell_2 \rightarrow BC\ell_2 + C\ell$$

now in progress, suggest a rate coefficient at 500 K about half that of

$$(5) \quad A\ell C\ell + C\ell_2 \rightarrow A\ell C\ell_2 + C\ell$$

with only a small temperature dependence for either reaction, compare Figure 1.
One of our long-term goals is to obtain comparisons of B-species reactions to
most of the $A\ell$ reactions shown in that figure; in other words, to prepare for
B-species reactions a comprehensive data compilation similar to Figure 1.

III. CUMULATIVE LIST OF PUBLICATIONS

1. D.F. Rogowski and A. Fontijn, "An HTFFR Kinetics Study of the Reaction
    Between $A\ell C\ell$ and O_2 from 490 to 1750 K," Twenty-first Symposium
    (International) on Combustion, in press.

2. D.F. Rogowski and A. Fontijn, "An HTFFR Kinetics Study of the Reaction
    Between $A\ell C\ell$ and CO_2 from 1175 to 1775 K," Chemical Physics Letters,
    132, 413 (1986).

3. D.F. Rogowski and A. Fontijn, "The Radiative Lifetime of $A\ell C\ell$ $A^1\Pi$,"
    Chemical Physics Letters, 137, 219 (1987).

4. A.G. Slavejkov, D.F. Rogowski and A. Fontijn, "An HTFFR Kinetics Study
    of the Reaction Between $BC\ell$ and O_2 from 540 to 1070 K," Chemical Physics
    Letters, in press.

5. D.F. Rogowski, P. Marshall and A. Fontijn, "High-Temperature Fast-Flow
    Reactor (HTFFR) Kinetics Studies of the Reactions of $A\ell$ with $C\ell_2$, $A\ell$ with
    $HC\ell$ and $A\ell C\ell$ with $C\ell_2$ Over Wide Temperature Ranges," The Journal of
    Physical Chemistry, in preparation.

IV. PROFESSIONAL PERSONNEL

Donald F. Rogowski and Aleksander G. Slavejkov performed the experimental work discussed in Section II. The former is expected to receive his Ph.D. in the near future. His research has been fully supported by AFOSR. Various people in our research group, particularly David A. Stachelczyk and William F. Flaherty, have been involved in the construction and testing of the mass-spectrometer-HTFFR apparatus.

V. PRESENTATIONS AND OTHER INTERACTIONS

We presented papers and seminars in which results of our AFOSR-sponsored work were discussed, at the:

1. Department of Chemistry, University of Toronto, Toronto, Ont. (May 1986).

2. McDonnell Douglas Research Laboratories, St. Louis, MO (May 1986).

3. AFOSR/ONR Contractors Meeting on Combustion, Stanford University, Stanford, CA (June 1986).

4. Twenty-First International Symposium on Combustion, Munich, W. Germany (August 1986).

5. Departments of Chemical Physics and Chemical Kinetics, S.R.I. International, Menlo Park, CA (October 1986).

6. Department of Applied Mechanics and Engineering Sciences, University of California at San Diego, La Jolla, CA (October 1986).

7. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD (May 1987).

8. Naval Research Laboratory, Washington, DC (May 1987).

9. AFOSR/ONR Contractors Meeting on Combustion and Rocket Propulsion, Pennsylvania State University, University Park, PA (June 1987).

10. Eighteenth Symposium on Free Radicals, Oxford, England (September 1987).

11. Chemical Thermodynamics Division, National Bureau of Standards, Gaithersburg, MD (November 1987).

12. American Institute of Chemical Engineers, Annual Meeting, New York City, NY (November 1987).

Dr. C.W. Larson of the Air Force Astronautics Laboratory, and other Air Force Personnel, contacted us several times in 1986 and 1987 to discuss the design of a high-temperature reactor for use in spectroscopic measurements on hydrogen/metal-vapor mixtures. They are interested in such information in the context of the Solar Plasma Propulsion Program. We maintain periodic contacts with Dr. David P. Weaver of that laboratory. Dr. J. Lurie, of Aerodyne Research Inc., called us to obtain information on our $A\ell C\ell$ radiative lifetime measurements for their plume model calculations for AEDC. Dr. M.W. Chase of the National Bureau of Standards had several discussions with us on the implication of our measurements for entries on aluminum species in the JANAF Thermochemical Tables. We have initiated some collaboration with Dr. J.R. McDonald's group at N.R.L., in connection with their BH compound combustion research and our mass spectrometric work. I (A.F.) have accepted an invitation to serve as a member of the ONR Board of Visitors for review of their Mechanics Division Program.

VI. REFERENCES

1. A. Fontijn and R. Zellner, "Influence of Temperature on Rate Coefficients of Bimolecular Reactions," Reactions of Small Transient Species. Kinetics and Energetics, A. Fontijn and M.A.A. Clyne, Eds. (Academic Press, London, 1983), Chap.1.

2. D.F. Rogowski, A.J. English and A. Fontijn, "An HTFFR Kinetics Study of the Reaction $A\ell O + CO_2 \rightarrow A\ell O_2 + CO$. Thermochemical Implications," J. Phys. Chem. 90, 1688 (1986).

3. P. Ho and R.P. Burns, "A Mass-Spectrometric Study of the $A\ell O_2$ Molecule," High Temp. Sci. 12, 31 (1980).

4. J.B. Lurie and C.E. Kolb, Private communication to A. Fontijn on work done for AEDC, May 1987.

5. D.F. Rogowski and A. Fontijn, "An HTFFR Study of the Reaction Between $A\ell C\ell$ and O_2 from 490 to 1750 K," Twenty-first Symposium (International) on Combustion, in press.

6. D.F. Rogowski and A. Fontijn, "An HTFFR Kinetics Study of the Reaction Between $A\ell C\ell$ and CO_2 from 1175 to 1775 K," Chem. Phys. Lett. 132, 413 (1986).

7. D.F. Rogowski and A. Fontijn, "The Radiative Lifetime of $A\ell C\ell \ A^{1}\overline{..}$," Chem. Phys. Lett. 137, 219 (1987).

8. A. Fontijn, "Temperature Dependence of the Kinetics of Elementary Combustion Reactions of Refractory Species," Combust. Sci. and Tech. 50, 151 (1986).

9. A. Fontijn, Final Report on Grant AFOSR-82-0073, January 1986.

10. A.G. Slavejkov, D.F. Rogowski and A. Fontijn, "An HTFFR Kinetics Study of the Reaction Between $BC\ell$ and O_2 from 546 to 1670 K," Chem. Phys. Lett., in press.

11. G.C. Light, R.R. Herm and J.H. Matsumoto, "Kinetics of Some Gas-Phase Elementary Reactions of Boron Monofluoride," J. Phys. Chem. 89, 5066 (1985).

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